Interatomic forces for transition metals including magnetism

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Abstract

We present a formalism for extending the second moment tight-binding model[1], incorporating ferro- and anti-ferromagnetic interaction terms which are needed for the FeCr system. For antiferromagnetic and paramagnetic materials, an explicit additional variable representing the spin is required. In a mean-field approximation this spin can be eliminated, and the potential becomes explicitly temperature dependent. For ferromagnetic interactions, this degree of freedom can be eliminated, and the formalism reduces to the embedded atom method (EAM[2]), and we show the equivalence of existing EAM potentials to "magnetic" potentials.

Introduction

Ferritic stainless steels have good radiation resistance are good candidates for use in many nuclear applications. A fundamental understanding of their properties under radiation and ageing can be obtained by molecular dynamics (MD) and Monte Carlo (MC) simulations. The crucial ingredient for such studies is a model of the forces between atoms: the interatomic potential.

While commercial stainless steels are typically multicomponent, the major components are iron and chromium, which exhibit ferro- and antiferromagnetism. Early work neglected explicit treatment of magnetism [3, 4, 5, 6, 7, 8, 9] or was confined to a lattice[10, 11] since the Curie temperature T_C of body-centred cubic (bcc) iron is 1043 K, this is a serious approximation. Ab initio studies show that magnetic interactions between the atoms can have a major effect on defect energetics, e.g. the vacancy formation energy changes by up to 40% with different magnetic states. [12].

A simple way to include magnetic effects involves defining environment-dependent localised magnetic moments in total energy expressions[13, 14, 15]. Here we extend this work and outline a framework to develop a model treating magnetic and non-magnetic Fe-Fe interactions in arbitrary configurations based on the 2nd moment approximation of tight-binding.

Magnetism in the 2nd moment approach

Band Energy

We base our work on the second moment approximation to tight binding[3], extended to multiple bands s, and two $d-$bands of opposite spin. In the two-band model the contribution to the cohesive energy from the d-bands is proportional to the square root of the bandwidth, which is approximated by a sum of pairwise potentials [3]. By assuming local charge neutrality[16] and charge transfer between bands[19, 8] multiple bands and arbitrary atomic numbers can be treated.

Consider a rectangular single spin band containing N states of full width W centred on the free atom eigenvalue (assumed degenerate). Electrons occupy the lower energy states, so relative to the free atom the cohesive energy is given by:

$$U = \int_{-W/2}^{E_f} \frac{5E}{W} dE = Z \left(\frac{Z}{5} - 1 \right) \frac{W}{2} \tag{1}$$

where Z is the occupation of the band and the Fermi energy is $E_f = (Z/N - 1/2)W$. By defining a local density of states projected onto an atom, this becomes an expression for energy per atom. If we consider a single band, Z is constant for a given material, and the cohesive energy varies parabolically with the number of d-electrons. In the second moment approach, the bandwidth W can be written as the square root of a sum of pairwise potentials, which following Finnis and Sinclair[3] we assume can be empirically fitted to data.

$$W_{b,i} = \sqrt{\sum_j \phi_b(r_{ij})} \tag{2}$$

where the fitting function $\phi_b(r_{ij}$ is a measure of the strength of the bond. In transition metals, the cohesion arising from d-band formation is expected to dominate, but the contribution from s-band formation may not be negligible [20]

To include magnetism, we assume two local d-band densities of states (N=5) with opposite spins, labelled by arrow, and one s-band (N=2). Writing down the second moment energy for three bands, one finds

$$E^{band} = U^\uparrow + U^\downarrow + U^s = W_d \left[\frac{n_d^2 + \mu^2}{20} - \frac{n_d}{2} \right] + W_s \left[\frac{n_s^2 - 2n_s}{4} \right] \tag{3}$$

where $n_d = Z^\uparrow + Z^\downarrow$ is the total number of d-electrons, n_s is the number of s electrons. The valence is then $n_d + n_s$. It is assumed that both d-bands have the same width W_d, regardless of occupation. The on-site magnetic moment (in units of Bohr magnetons) is then $\mu = Z^\uparrow - Z^\downarrow$.

This band formation contribution to the magnetic energy is always positive. It can be shown that by a simple shift of variables it can be implicitly included in the many-body part of second-moment potentials. This makes the "Embedding function" somewhat more complicated than the standard square root of Finnis-Sinclair type potentials, and helps explain the surprising success of previous EAM potentials developed for iron [3, 5, 6].

Many-body repulsion

In order to construct a potential usable in MD we need to add non-magnetic repulsive terms to the total energy expression. At equilibrium, s-band electrons contribute significantly to pressure and in particular bulk modulus [20]. Further, due to wavefunction overlap causing a shift of the centre of the d-band, d-electrons also contribute to repulsion small distances, although since d-orbitals are quite compact for transition metals this is expected to be small. We therefore write for the on-site non-magnetic 2nd moment band energy:

$$E^{nm} = E_d^{rep} + E_s^{rep} + (2 - n_s)E_{s \to d} \tag{4}$$

where l_b is the orbital angular momentum of band b, E_b^{rep} represents many-body repulsive interactions. $E_{s \to d}$ is the energy required to promote an s-electron to the d-level in the free atom, a term which must be included if $s - d$ transfer is allowed.

One possibility is that the many body repulsion term is approximated by the kinetic energy of a free electron gas, where the local density may be measured by a sum of pair potentials, similar to the bandwidth.

$$E_{b,i}^{rep} = n_b^2 \rho_{b,i}^{5/3}; \qquad \rho_{b,i} = \sum_j \phi_b^{rep}(r_{ij}) \tag{5}$$

Note that the function ϕ_b^{rep} will be different from ϕ_b in equation 2. It is expected that the s-electrons will give the major contribution. The repulsion due to kinetic energy of d-electrons is expected to be considerably smaller than the Pauli exclusion of d-electrons with spins aligned in the same direction.

Magnetic energy

So far we have not considered interaction between spins, arising from Pauli repulsion (exchange) and correlation. This should have both on-site and inter-site terms. Expanding about the non-magnetised state, we choose a Landau-Ginzberg expansion for the on-site terms:

$$E_i^I = -\frac{I_2}{4}\mu_i^2 + \frac{I_4}{8}\mu_i^4 \tag{6}$$

Where I_2 and I_4 are *on-site* spin-polarisation parameters following a Landau-Ginzberg expansion and E^{xc} is the *intersite* exchange-correlation energy. Partitioning into pairwise contributions from repulsive Pauli exclusion between like-spin electrons $\mathcal{J}_P(r_{ij})$ and Heisenberg correlation $\mathcal{J}_c(r_{ij})$ gives

$$
\begin{aligned}
E_i^{xc} &= \frac{1}{2}\sum_j \left[\mathcal{J}_P(r_{ij})\left(Z_i^\uparrow Z_j^\uparrow + Z_i^\downarrow Z_j^\downarrow \right) + \mathcal{J}_c(r_{ij})\mu_\mathbf{i}\mu_\mathbf{j} \right] \\
&= \frac{1}{2}\sum_j \left[\mathcal{J}_P(r_{ij})\frac{(n_d^i n_d^j)}{2} + \left(\frac{1}{2}\mathcal{J}_P(r_{ij}) + \mathcal{J}_c(r_{ij}) \right)\mu_\mathbf{i}\mu_\mathbf{j} \right]
\end{aligned} \tag{7}
$$

where n_d is the number of d-electrons in the solid. These *off-site* exchange-correlation interaction terms are essential for modelling of Curie and Neel transitions as well as negative mixing energies from frustration of anti-ferromagnetically aligned solute atoms, such as Cr in Fe[17, 18].

The spins may be treated either dynamically (fictitious dynamics) or statically (Born-Oppenheimer approximation). For the latter case differentiating $E_i^{band} + E_i^I + E_i^{xc}$, shows that the on-site magnetic moment μ_i is stationary in a perfect lattice (i.e. $|\mu_\mathbf{i}| = \mu$) when

$$\mu_i^2 = \frac{1}{I_4}\left[I_2 - \left(\frac{W_{d,i}}{5} + \sum_j \left[\frac{1}{2}\mathcal{J}_P(r_{ij}) + \mathcal{J}_c(r_{ij}) \right] \right) \right] \tag{8}$$

In the free atom limit $r \to \infty$, Hund's rule must be satisfied $\mu = \mu_{free} = 5 - |5 - n_d|$, and the energy should be a minimum for this magnetic moment. This gives us a relation between the Landau-Ginzburg expansion coefficients and the free atom properties:

$$I_2 = 8E_{free}/\mu_{free}^2; \qquad I_4 = 8E_{free}/\mu_{free}^4$$

where E_{free} is the energy difference between non-magnetic and magnetic free atom. E_{free} and μ_{free} are both numbers, easily measured from the free atom properties.

A further simplification can be made using the Born-Oppenheimer approximation: the magnetisation is in the ground state for a given atomic configuration, and we may assume that $\partial E/\partial \mu = 0$. This leads to

$$\mu_i = \mu_{free}\sqrt{1 - \frac{\mu_{free}}{8E_{free}}\left(\frac{W_{d,i}}{5} + \sum_j \mathcal{J}(r_{ij})\right)} \tag{9}$$

where $\mathcal{J} = \frac{1}{2}\mathcal{J}_P + \mathcal{J}_c$; the two separate physical effects are merged in a single pairwise interaction. Equation 10 shows that as the canonical d-band broadens, lowering the band energy, so the magnetic moment is reduced. Thus the magnetic moment in the solid is significantly lower than the free atom, the moment around a vacancy is enhanced, and the moment around an interstitial defect is further suppressed.

Total Energy

Collecting together the terms discussed above, the final form of the energy for our modified second moment three band model with both on and off site magnetism is $E_{tot} = \sum_i E_i$, with:

$$
\begin{aligned}
E_i &= W_{d,i}\left[\frac{n_d^2 + \mu_i^2}{20} - \frac{n_d}{2}\right] + E_{d,i}^{rep} \\
&+ W_{s,i}\left[\frac{n_s^2}{4} - \frac{n_s}{2}\right] + E_{s,i}^{rep} + (2 - n_s)E_{s\to d} \\
&+ \frac{1}{4}\sum_j \mathcal{J}_P(r_{ij})n_d^i n_d^j + \frac{1}{2}\sum_j \mathcal{J}(r_{ij})\mu_i\mu_j \\
&- \frac{E_{free}^\mu}{8}\left[\mu_i^2 - \frac{\mu_i^4}{2\mu_{free}^2}\right].
\end{aligned} \tag{10}
$$

Once again $\mathcal{J} = \frac{1}{2}\mathcal{J}_P + \mathcal{J}_c$. The model has numerical parameters Z, $E_{s\to d}$, E_{free}^μ, requires pair potentials for $W_{b,i}$, $a_b^{rep}\phi_b(r_{ij})$, $\mathcal{J}_P(r_{ij})$ and $\mathcal{J}(r_{ij})$. It is interesting to note that the s-band contributes to the bonding thanks to the $s \to d$ transfer in the solid. This increases the number of d-electrons, potentially increasing the magnetic moment for elements with valence less than 7, and reducing it for atoms with valence above 7.

Analytic expressions for charge transfer

It is possible to treat n_d and n_s as variables, or to use the Born-Oppenheimer Approximation and solve for n_d and n_s as minimisers of the energy. For the latter approach, we take the case of iron and differentiate the total energy (10) with respect to n_s, under the condition $n_d = 8 - n_s$. In a perfect lattice with zero net magnetic moment n_s is equal on all atoms i, we obtain :

$$n_s = \frac{W_s + \frac{3}{5}W_d + 8\sum_j \mathcal{J}_p(r_{ij}) + 8\rho_d^{5/3} + 2E_{s\to d}}{W_s + \frac{1}{5}W_d + \sum_j \mathcal{J}_p(r_{ij}) + 4\rho_s^{5/3} + 4\rho_d^{5/3}} \tag{11}$$

For magnetic states, the expression for n_s becomes more complex:

$$n_s = \frac{\dfrac{W_s + \frac{3}{5}W_d + 8\sum_j \mathcal{J}_{P,ij} - 4\sum_j \mathcal{J}_{ij} + 8\rho_d^{5/3} + 2E_{s\to d}}{\frac{1}{2}E_{free}^\mu + \left(6(\sum_j \mathcal{J}_{ij})^2 + \frac{4}{5}\sum \mathcal{J}_{ij} - \frac{2}{25}W_d^2\right)/E_{free}^\mu} + 1}{\dfrac{W_s + \frac{1}{5}W_d + 2\sum_j \mathcal{J}_{P,ij} + 4\sum_j \mathcal{J}_{ij} + 4\rho_s^{5/3} + 4\rho_d^{5/3}}{\frac{1}{2}E_{free}^\mu + \left(6(\sum_j \mathcal{J}_{ij})^2 + \frac{4}{5}\sum \mathcal{J}_{ij} - \frac{2}{25}W_d^2\right)/E_{free}^\mu} - 1} \tag{12}$$

This expression only applies in the homogeneous case, a mean-field approximation when $\mu_i = \mu_j$. Otherwise determining the $s - d$ transfer is non-local, and best treated by fictitious dynamics with n_s and μ as dynamical variables. However, provided $\mu_i \approx \mu_j$ the error is only second order. To show this we can go to the low temperature limit where $\mu_{\mathbf{i}}.\mu_{\mathbf{j}} = \pm\mu_i\mu_j$:

$$
\begin{aligned}
\mu_{\mathbf{i}}.\mu_{\mathbf{j}} &= \frac{(\mu_i + \mu_j)^2 - \mu_i^2 - \mu_j^2}{2} \\
&= \frac{(2\mu_i + \delta\mu_{ji})^2 - \mu_i^2 - \mu_j^2}{4} + \frac{(2\mu_j + \delta\mu_{ij})^2 - \mu_i^2 - \mu_j^2}{4}
\end{aligned}
\tag{13}
$$

where $\delta\mu_{ij} = \mu_i - \mu_j$ Now we can use the fact that the energy per atom is an arbitrary quantity to assign terms in μ_j^2 to E_j, making them local. Further the cross term becomes

$$
\mu_j.\delta\mu_{ij} + \mu_i.\delta\mu_{ji} = (\delta\mu_{ij})^2
$$

i.e. second order in the difference in spin. Thus the effect of inhomogeneities on n_s is small. At higher temperature the coupling term becomes even smaller.

With this redistribution of energy between atoms, we find

$$
\sum_{ij} \mathcal{J}(r_{ij})(\mu_{\mathbf{i}}.\mu_{\mathbf{j}}) = \sum_{ij} \mathcal{J}(r_{ij})(\mu_i^2 - \frac{1}{2}\delta\mu_{ij})
\tag{14}
$$

To use the analytic expression for charge transfer, one has to ignore the $\frac{1}{2}\delta\mu_{ij}$.

Forces

There are two approaches to applying the current model to MD. For the model with a full seven degrees of freedom per atom, one simply writes a Lagrangian including n_s and μ at each atom, defines fictitious masses to each, and integrates the equations of motion. However, it is desirable to avoid explicitly including extra degrees of freedom.

The Hellmann-Feynman theorem tell us that to evaluate forces we do not have to consider partial derivative with respect to variational parameters. Here, in the Born-Oppenheimer approximation μ_i, n_s and n_d all fall into this category. Thus the force is

$$
\begin{aligned}
\mathbf{F_i} &= -\frac{dE}{d\mathbf{r_i}} \\
&= -\frac{\partial E}{\partial \mathbf{r_i}} - \frac{\partial E}{\partial n_s}\frac{\partial n_s}{\partial \mathbf{r_i}} - \frac{\partial E}{\partial n_d}\frac{\partial n_d}{\partial \mathbf{r_i}} - \frac{\partial E}{\partial \mu_{\mathbf{i}}}\frac{\partial \mu_{\mathbf{i}}}{\partial \mathbf{r_i}} \\
&= -\frac{\partial E}{\partial \mathbf{r_i}}
\end{aligned}
\tag{15}
$$

Consequently, although the analytic solution for the energy in the Born-Oppenheimer approximation is cumbersome, it yields tremendous simplification of the forces.

Equivalence to and comparison with two-band and magnetic potentials

If we take a filled s band, n_s=2, neglect the intersite interaction and take a pairwise potential rather than Fermi-gas approach to the repulsive terms then we obtain the "magnetic" potential[13]. Similarly, the proof that the two-band magnetic model reduces in the

Born-Oppenheimer approximation to EAM[14] can be trivially applied here under the same assumptions.

Although previous EAM parameterisations for iron have not explicitly included magnetism, since they are fitted to data which does include magnetism, it should be possible to reverse engineer the atomistic magnetic moment from any EAM potential. We have shown here that it is simply a function of the d-band width, so we need only find the relevant relationship..

In figure 1 we show a comparison between atomic magnetic moments calculated from first principles in iron[21, 22] and bandwidth from an EAM iron potential [6]. Also shown is the equivalent figure for the Dudarev-Derlet magnetic potential[13]. The similarity between the two is striking, but more interesting is the fact that the data does not fit well to a single function of bandwidth. It appears that a single nearby interstitial has a much greater effect on suppressing the magnetisation than it does in increasing the local bandwidth. Closer examination of the projected d-band density of states suggests that its shape is changed by point defects, but not by compression. Since the shape of the band is not properly captured in second moment models.
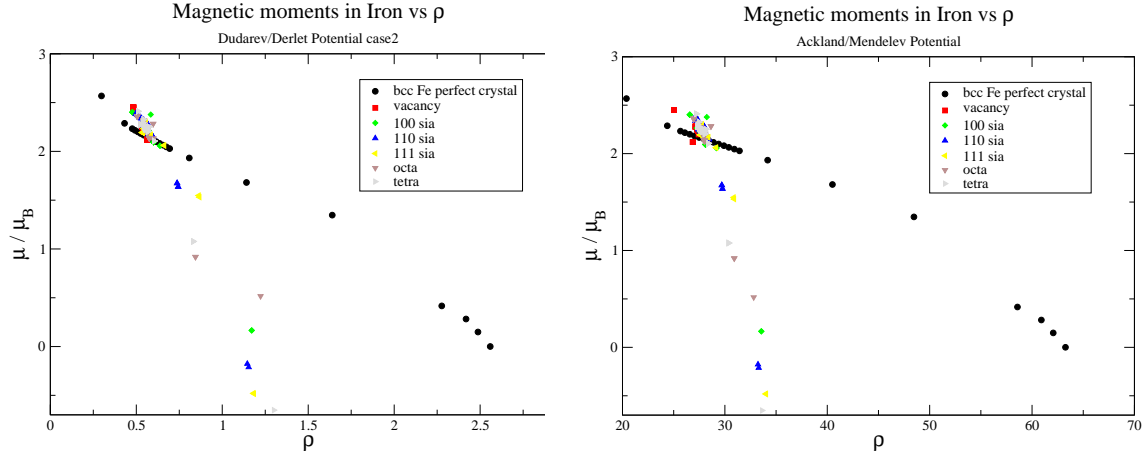

Figure 1: Graphs of magnetic moment against ρ (W^2) for Mendelev and Dudarev potentials. Symbols represent isotropic compression of bcc Fe, and sites close to point defect configurations including self interstitials in tetrahedral, octahedral and three dumbbell configurations

Simplification: Elimination of the s-d electron transfer

Computationally, the slowest part of the potential is the s-band. This is because of the long range of the functions. In practice, the s-band occupation is relatively insensitive to the atomic positions, and only weakly dependent on the density, and for simulation of solids it is possible to fix the s-electron occupation without changing the results. This also has the significant advantage that the only variable which needs to be optimised is the magnetisation: n_d is constant. On account of its partial occupancy, the s-band still contributes significantly to the cohesive energy, an effect ignored by previous models, but its long range means it has little effect on structural properties. Fixing n_s has the important practical advantage that the μ_i can be determined algebraically. This is only likely to be problematic when considering properties involving the free atom, e.g. cohesive energy or sputtering.

A still further simplification eliminates the s-band terms altogether. In a practical molecular dynamics simulations, for a reasonably homogeneous system, the free-electron s-band

width can be written a simple non-local function of density, taking the same value for all atoms. In a constant volume simulation, this will be the same for all time, and simply add a constant term to the cohesive energy and bulk modulus. It suffers from the problem that the bulk modulus associated with volume change is different from that calculated from the limit of long-wavelength phonons (and therefore one needs to decide which to fit), but in many practical applications this may be unimportant.

Simplification: Decoupling the magnitude and coupling of μ

The time and energy scales for rotation of the spins are much smaller than for changes in spin magnitude or atomic position. This means we can obtain some simplification by integrating out the rotational degrees of freedom.

The intersite spin term, $\mathcal{J}(r_{ij})\mu_\mathbf{i}.\mu_\mathbf{j}$, couples spins on adjacent sites. This makes the task of evaluating ground state for the full set of spins $\{\mu_I\}$ nonlocal and slow: in practice it is more sensible to evaluate the spin degrees of freedom explicitly and dynamically[15]. It is possible, however, to greatly simplify the potential by making a pairwise approximation for the spins. Here we store only the magnitude of the spins on each site, and replace the explicit dot product with its ensemble average, treating each "bond" independently.

$$\mu_\mathbf{i} \cdot \mu_\mathbf{j} \quad \rightarrow \quad \frac{\int \mu_i\mu_j \cos\theta e^{\mathcal{J}\mu_i\mu_j \cos\theta/kT} \sin\theta d\theta d\phi}{\int e^{\mathcal{J}\mu_i\mu_j \cos\theta/kT} \sin\theta d\theta d\phi} \tag{16}$$

$$= \quad \coth\left(\frac{J\mu_i\mu_j}{kT}\right) - \frac{kT}{J\mu_i\mu_j} \tag{17}$$

The advantage of this approach is twofold: it reduces the degrees of freedom from 6N to 4N, and by treating the fastest processes implicitly it allows one to use a larger timestep. A curious feature is that the potential becomes explicitly temperature dependent. Unlike simple magnetic potentials[13, 14, 23] it still allows one to distinguish local ferromagnetic and antiferromagnetic behaviour, but not antiferromagnetic frustration.

Conclusions

We have presented a formalism within which magnetism can be treated within the second moment approximation to tight binding, a Heisenburg model for spin-coupling and and a Landau-Ginzberg approximation for onsite spins. The model is mathematically complicated, at worst requiring four additional variables (n_s and a vector spin) per atom. We have also shown, however, that these variables can be eliminated with well controlled approximations. Computationally, the model is efficient, requiring only the evaluation of short range pair potentials for forces or energies.

Parameterisation of the model is a significant undertaking. In principle the various parameters and pair potentials must be fitted for each element on pair of elements. It may prove that similar functions apply across the whole group[24], and the division of the energy into magnetic and non-magnetic parts allows data calculated using either method from first principles to be used. The combination of a mean-field approach to the inter-site magnetism, the Born-Oppenheimer approximation for the spin degree of freedom and the Hellmann-Feynman theorem for forces reduces the model to a temperature-dependent EAM, albeit with more than one embedding term.

The model automatically reproduces a number of features of transition metal binding: band formation, magnetism, $s - d$ charge transfer, suppression of magnetism in forming a solid, further suppression of magnetism in overcoordinated defects and increased cohesion for elements in the centre of the d-series. Since each term has a well-defined physical interpretation within the local density of states in tight-binding band theory, results from the model provide physical intuition as well as numerical predictions.

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